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**APPLICATION NUMBER:** ***60/545,139***
**FILING DATE:** ***February 18, 2004***
**RELATED PCT APPLICATION NUMBER:** ***PCT/US05/04567***

UNITED STATES PATENT AND TRADEMARK OFFICE
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# PROVISIONAL APPLICATION FOR PATENT COVER SHEET

**This is a request for filing a PROVISIONAL APPLICATION FOR PATENT under 37 CFR 1.53(c).**

22154 U.S. PTO
60/545139
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☐ *Additional inventors are being named on the_____ separately numbered sheets attached hereto*

**TITLE OF THE INVENTION (280 characters max)**

A NANOSCALE METAL PASTE-DISPERSED USING ULTRASONIC METHOD--AS AN ELECTRICAL THERMAL INTERFACE MATERIAL FOR ELECTRONIC PRODUCTS

*Direct all correspondence to:* **CORRESPONDENCE ADDRESS**

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**ENCLOSED APPLICATION PARTS** ***(check all that apply)***

☒ Specification *Number of Pages* 4
☒ Drawing(s) *Number of Sheets* 10
☐ Application Data Sheet. See 37 CFR 1.76
☐ CD(s), Number
☐ Other (specify)

METHOD OF PAYMENT OF FILING FEES FOR THIS PROVISIONAL APPLICATION FOR PATENT *(check one)*

☒ Applicant claims small entity status. See 37 CFR 1.27.
☒ A check or money order is enclosed to cover the filing fees
☒ The Director is hereby authorized to charge filing fees or credit any overpayment to Deposit Account Number: **50-2041**
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The invention was made by an agency of the United States Government or under a contract with an agency of the United States Government.

☐ No.
☒ Yes, the name of the U.S. Government agency and the Government contract number are: **Through NSF through CPES**

*Respectfully submitted,*

Date **2-18-04**

SIGNATURE

REGISTRATION NO. *(if appropriate)* **32,635**

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Docket Number: **01640448PR**

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## USE ONLY FOR FILING A PROVISIONAL APPLICATION FOR PATENT

# A NANOSCALE METAL PASTE-DISPERSED USING ULTRASONIC METHOD-AS AN ELECTRICAL AND THERMAL INTERFACE MATERIAL

All semiconductor chips have to be fastened or attached to a substrate to function in an electronic product. The state-of-the-art technology for interconnecting these chips typically uses a lead or lead-free solder alloy or polymeric glues, like epoxy. These materials have poor thermal properties to dissipate the heat generated by the chips, poor electrical properties to reduce loss of electrical power, and poor robustness for mechanical strength and reliability. Furthermore, because of the low melting temperatures of solder alloys and low decomposition temperatures of epoxies, they are not suitable for allowing some chips (like SiC or GaN chips) to function at high temperatures. This invention involves the development of a metallic material that has very fine particles. The material can be applied and processed like a solder paste or epoxy. The properties (thermal, electrical, and mechanical) of the joint formed with this new material are far superior to those of solder or epoxy. This material has a wide range of applications. It can be used to bond silicon integrated-circuit chips in computers, or silicon power chips in power suppliers, or optoelectronic chips in telecommunication modules. Also, since the metal melts at a temperature over 800°C, it is also suited for attaching semiconductor chips that can be operated at high temperatures, e.g., SiC or GaN power chips. The ability to allow these chips to operate at high temperatures cuts down their cooling requirement, leading to savings in materials and energy in the manufacture and operations of the product.

In order to fasten electronic components, especially high-temperature devices such as SiC to substrates, a connecting layer having good electrical and thermal conductivity and good adhesion is fabricated by sintering nanoscale metal paste. Sintering of microscale metal powder paste is commonly used in hybrid electronic packages for producing electrical circuit patterns. However, the high processing temperatures (>600°C) prevents its used in joining electronic components to substrates. The current practice is to use solder that is reflowed at temperatures low enough for the devices to withstand. The advantage of low melting temperature becomes a liability for solder alloys because they can not meet the requirements of high temperature application. Furthermore, solder materials have relatively poor electrical and thermal properties and fatigue resistance compared to other metals such as copper and silver, which detrimentally

affect the performance of the whole electronic system. Sintering nanoscale metal paste is a viable solution because it enables the circumvention of the high processing temperature required for micrometer-size metal powder.

**The preferred metal is silver because of a combination of low cost (as compared to gold) and the amenability of being fired in ordinary atmosphere. While it is processed at temperatures comparable to that of solder reflow, it can withstand subsequent exposure to higher temperature, which solder cannot. The general process of microscale metal paste sintering can be directly applied to nanoscale paste with few changes. The nanoscale metal powder can be easily prepared using known techniques such as the Carey Lea method where the metal ions are rapidly reduced to nanopowder in solution, which is then recovered by separating the spent solution from the solids, by such method as centrifuging. Alternatively, it can be obtained from a number of commercial vendors at a cost comparable to that of micron-size powder. The current practice of applying the metal paste to substrates and surfaces is by screen or stencil printing. In order to form the paste, a binder system must be added to the nanopowder and mixed to a consistency that is suitable for printing and firing into a solid body with uniform structure. The binder properties (e.g., volatilization temperature) must match the sintering kinetics of the nanopowder and the temperature limitations imposed by the device being attached. The preferred binder is a low-boiling organic such as terpineol, with a boiling point below 220°C that enables unhindered densification of the powder at up to 300°C. To reduce viscosity, a thinner (such as RV 912 from Heraeus, Inc.) may be added. The total terpineol and thinner addition may be up to 20%. Dispersion of the metal in the binder system is aided by immersion in an ultrasonic bath using a room-temperature or cold water bath to prevent heating and sintering of the metal powder.**

The nanoscale silver paste should possess good screen/stencil printing properties to form the thick film. The typical thickness of the film formed by this method is at least 4 micrometers. In order to form a good bond, the substrate should be coated with a very thin layer of noble metal (silver or gold), especially when firing in ordinary atmosphere, because the paste lacks fluxing agents typically present in solder paste. After printing the metal paste on the substrate, the device is placed on top of the print and pushed down during the firing process to encourage good bonding through intimate contact. The fastening process is carried out at a temperature of 250°C or higher and for at least 2 minutes until the bond forms. The polymeric materials (binder and thinner) are volatilized prior to the occurrence of rapid coalescence among the nanoparticles at the higher temperature stage.

5. What is the existing technology/art to which you are comparing?
    1. Solder-reflow die-attach technique,
    2. Pressure-assisted sintering of metal paste

6. How does your INVENTION differ from present technology, what problems does it solve, or what advantages does it possess? (This should be written so someone skilled in the art can understand it.)

The sintered nanoscale silver offers improved electronic component joint (better electrical and thermal properties and fatigue resistance) while utilizing existing processing techniques and facilities at a cost comparable to those of sintered micron-size metal powder. It can be utilized for joining silicon devices while at the same time offering a unique solution for the joining of high-temperature electronic components.

Traditional silicon device-based electronic systems, which can only operate at temperatures below 125°C, cannot meet the requirement of next generation smart electronic system, such as remote actuators, point-of-use power supplies, and distributed high power control systems. Silicon carbide (SiC) and other wide-band gap semiconductors, such as gallium nitride (GaN) and diamond, are capable of operating efficiently at high temperatures. Recent studies have shown that SiC devices have favorable switching characteristics and the ability to function at elevated temperatures up to 350°C [1-3]. Being able to harness these devices would mean simpler and less costly cooling requirements, and improved system reliability. However, interconnecting these devices into an electronics circuit is a challenge in itself. The current technology for interconnecting power devices typically involves attaching one terminal of the semiconductor die to a heat-sinking substrate with a solder alloy and wire-bonding fine aluminum wires to the other terminal(s). Such an interconnect technology is not able to meet the high-temperature application requirement of the wide-band gap devices because of the low-melting points of solder alloys. Our invention makes use of the higher melting temperature silver in the form of nanopowder metal paste, which can be processed at low temperature and but retains high temperature resistance.

Pressure-assisted sintering uses commercial silver metal paste to attach the electronic components [4-5]. The metal powder typically has a particle size in the micrometer range. Because of the large particle size, a high sintering temperature is required (600°C and up) under normal firing conditions. At reduced firing temperature, a large pressure is applied on the assembly to assist the sintering process. However, the application of pressure can be undesirable because of increased difficulty in manufacturing with a corresponding increase in the production cost. Applying pressure also increases the likelihood of damage to the device during processing. By using metal particles in the nanoscale range, it is possible not only to reduce the bonding temperature but also to eliminates the need for high applied pressure. Without the need for high applied pressure, it is thus possible to make use of existing hybrid microelectronics processing techniques and fabrication equipment and therefore enable mass manufacturing of such components. The nanopowder can be easily prepared or purchased directly at a price comparable to that of micron-size powder and mixed with commercially available polymer binder of sufficiently low volatilization temperature. Dispersion of the powder in the binder can be facilitated by ultrasonic method in conjunction with other mechanical methods.

7. If not indicated previously, what are the possible uses and markets of the INTELLECTUAL PROPERTY? In addition to immediate applications, are there other uses that might be realized in the future?

Successful commercialization of the invention will provide solutions that will fill the gap in the technological development and application of high-temperature, high-performance, high-reliable electronic system and significantly impact the future growth of the trillion-dollar electronics industry.

Attach sketches, drawings, photographs, and other materials that may help illustrate the description. Rough art work, flow sheets, Polaroid photographs, and penciled graphs are satisfactory as long as they tell a clear and understandable story.

1. Nano-metal powder preparation:

The nano-metal powder can be made by using wet chemical methods wherein the dissolved metal ion is converted to metallic form by a hydride-based reducing agent. This method is useful for producing nanoparticles in the 10 to 30 nm range as shown in Fig. 1(a) where silver nanoparticles were obtained using a modified Carey Lea process. Fig.1 (b) proves that it is possible to sinter the silver powder at a significantly lower temperature such as 200°C. Alternatively, the powder is available as a commercial product from several vendors specializing in nanomaterials production at prices comparable to those of micron-size powder.

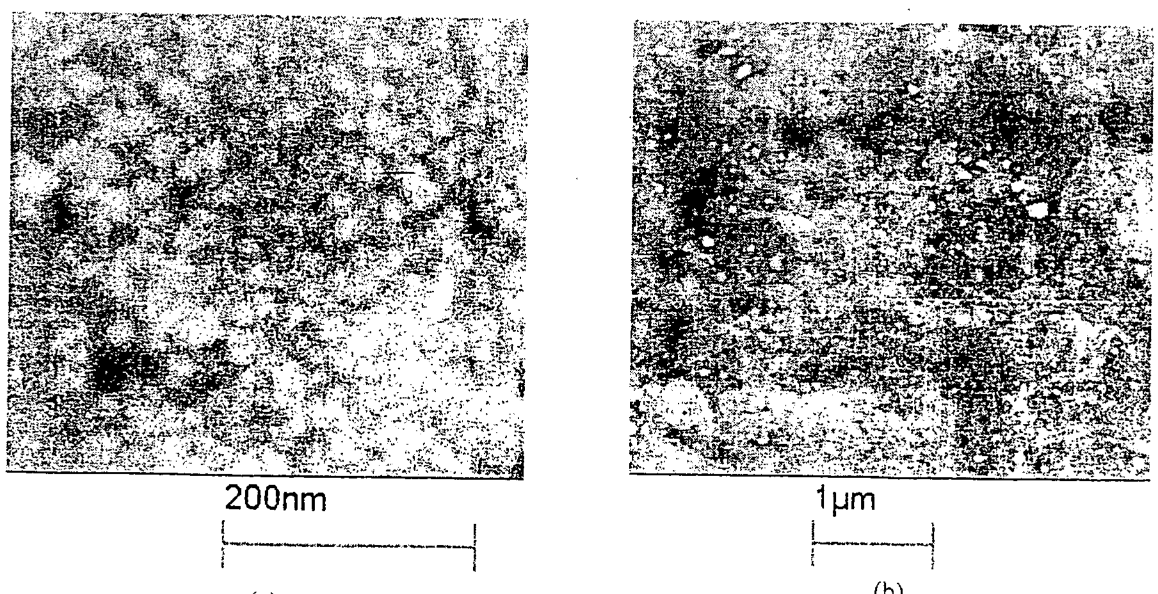



Figure 1. Nanosize silver prepared by the Carey Lea method (a) before sintering, and (b) after a 2 minute sinter at 200°C.

2. **Nanoscale silver paste preparation:**
**The nanoscale silver powder is converted to paste form by the addition of an organic solvent with low boiling point (e.g., terpineol) and thinner (e.g., RV 912 from Heraeus). The organics typically comprise up to 20% of the mixture. Dispersion of the powder was augmented by ultrasonic means in a cold water bath.**

3. **Electronic component attachment:**
**Electronic devices (silicon or wide bandgap devices) can be joined to substrates by sintering the nanopowder paste to form a solid bond layer between the devices and mounting substrate. Except for the low temperature used, it is similar to any other metal paste firing such as those performed for hybrid electronic packages. The firing temperature is comparable to solder reflow and only a moderate applied force is necessary to maintain intimate contact with the sintering metal powder layer. The nanoscale metal paste is typically screen or stencil printed on the substrate to form the thick film pattern onto which the device is mounted. After device placement, the die is pushed down with a moderate force and held in place while sintering takes place at a temperature of at least 250°C for 2 minutes or longer as required. The sintering procedure can be carried out in a conventional belt oven in a semi-continuous operation or in a box oven/furnace in a batch type operation.**

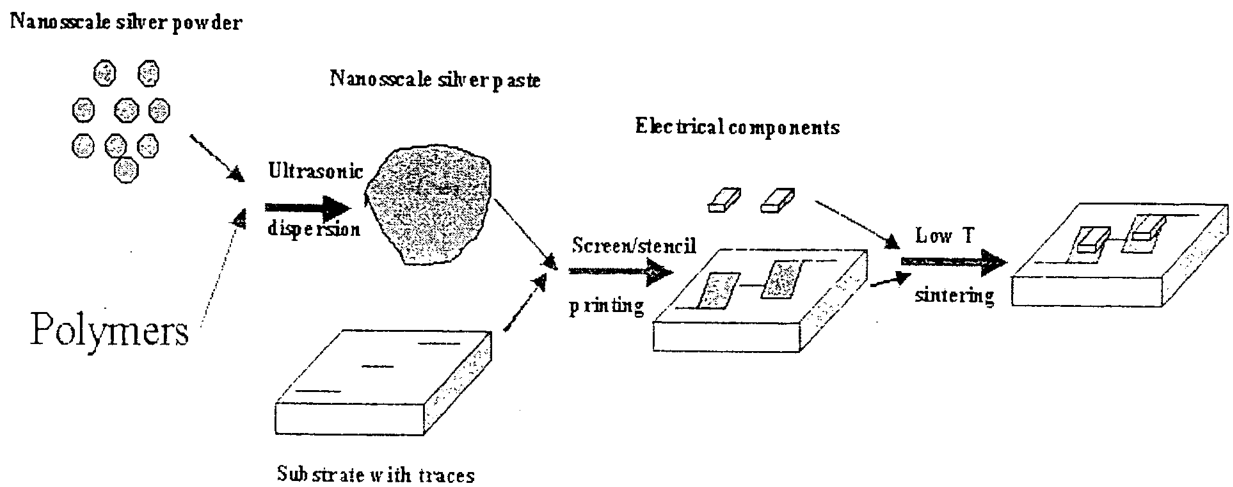
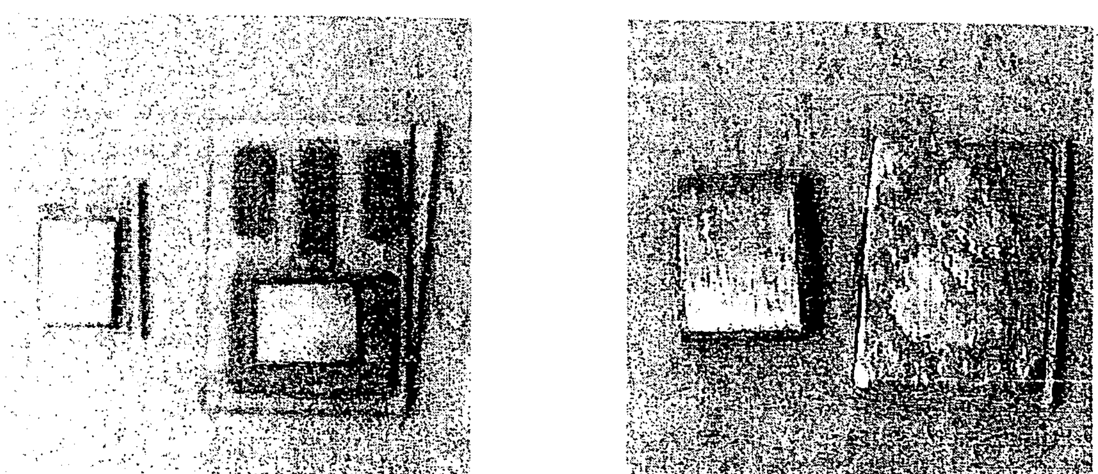



Figure 2.Schematic of low-temperature sintering nanoscale silver paste for electrical components attachment.



(a) (b)

Figure 3. (a) Silicon power devices attached to gold-plated direct bond copper (DBC) substrates with sintered nano-sized silver, and (b) separated device and substrate to show the silver die-attach layer.

Virginia Tech

# A Nanoscale Metal Paste - Dispersed Using Ultrasonic Method - as an Electrical and Thermal Interface Material for Electronic Products

## Update information for VTIP Disclosure No. 03.142

Virginia Tech, Blacksburg, VA

Inventors: Guo-Quan Lu, Zhiye (Zach) Zhang, Jesus N. Calata

Virginia Tech

# Market Potential

## Current market

- Roughly **60,000** tons of solder used each year in electronic device interconnection
- Estimated market value: 60,000 metric tons solder x 1000 kg/MT x 1000 gram/kg x \$0.5/gram = \$30 Billion.
- Solder joint failure accounts for **70%** of failures in electronic components.
- Limitation: not useful for products that operate at high temperatures such as high-power light emitting diodes (LED) for future lighting, lasers, power modules and high-temperature sensors.)
- Other issue(s): toxic; problem with waste disposal

## Opportunity:

- Silver is an attractive replacement for solder;
- Already used in the electronics industry (e.g., hybrid packages and ceramic capacitors)
- Environmentally friendly

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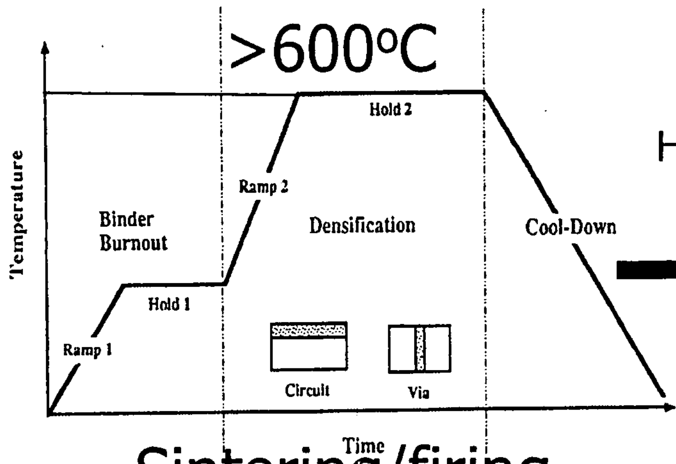
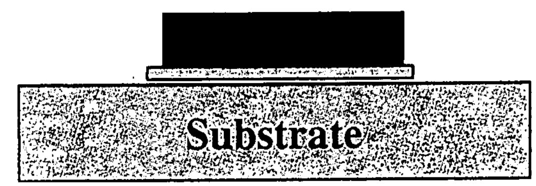
# ENABLING TECHNOLOGY FOR SILVER PASTES




Sintering/firing

High-T processing




Device interconnection

Problem: firing temperature is too high for devices

Our proposed solution: use nanoscale silver to replace micrometer-scale silver in paste

- firing temperature is within the limits of devices
- processing range is similar to that of solder
- can be used in existing SMT processes/equipment

Virginia Tech

# SOLDER REFLOW BACHGROUND

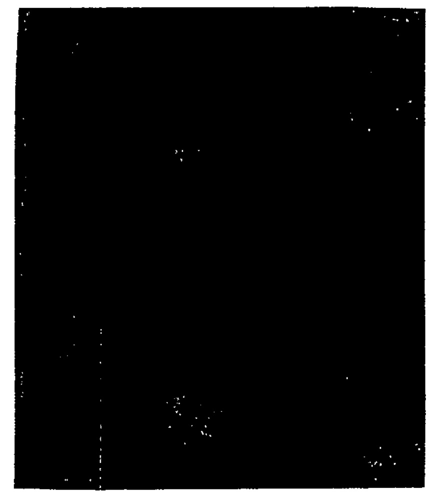
The state-of-art industry practice for device interconnection: **solder reflow**

Advantages: Low processing temperature (<300°C)

Disadvantages:

- Poor thermal, electrical and mechanical properties;
- Large voids causing thermal and reliability properties;
- Chip swimming in the liquid phase, alignment issue;
- High-temperature instable;
- Lead-contained solder causing environment issue.

| Property | Pb-Sn Solder | Cond. Epoxy | Cu | Ag |
|---|---|---|---|---|
| Elec. Condu. $\sigma$ (s/cm) | $2 \times 10^4$ -- $10^5$ | 0.01 -- $10^4$ | $5.8 \times 10^5$ | $6.7 \times 10^5$ |
| Therm. Conduc. $\kappa$ (W/m-K) | 40 -- 60 | 0.1 -- 10 | 339 | 419 |
| Adhes. to Cu (MPa) | 20 | ~ 20 | > 500 | > 140 |
| Melting Point (°C) | 120 - 350 | < 300* | 1080 | 961 |



Reflowed solder: large voids

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# WHY USE NANOSILVER PASTES?

- Low-temperature process and high-temperature application; (processing: <300°C, working :>600°C)
- Competitive cost; (comparable to conventional silver paste);
- Compatible process procedure; (existing device-interconnection processes and infrastructure can be directly applied to the nano-scale silver paste with little modification)
- Superior joint performance (electrical, thermal and mechanical properties);
- Significantly improved reliability;
- Reduced alignment problem during device attachment;
- Environment friendly (eliminates or reduces solder content in products).

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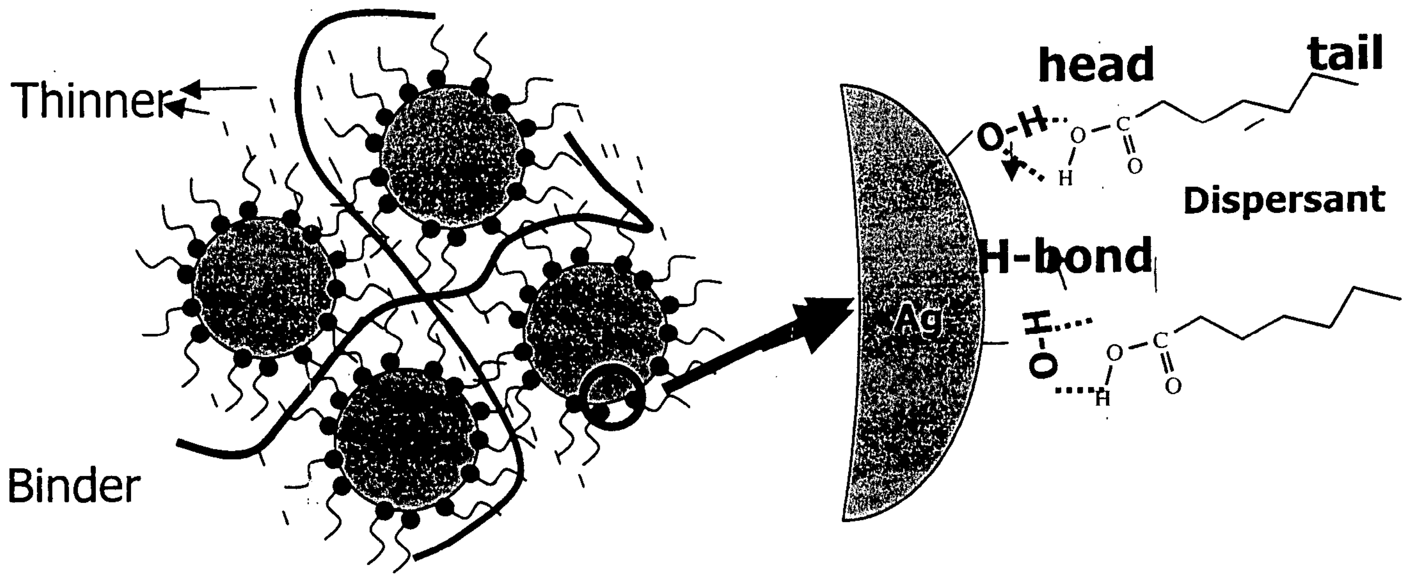
# REQUIREMENTS FOR MAKING THE PASTE




In order to disperse the nanosilver homogeneously to suitable for existing device interconnection technique three polymer vehicles are needed.

Dispersant: Disperse Silver Particles and Prevent Agglomeration.

Binder: Prevent Paste Crack during the Handling and Dry Processing.

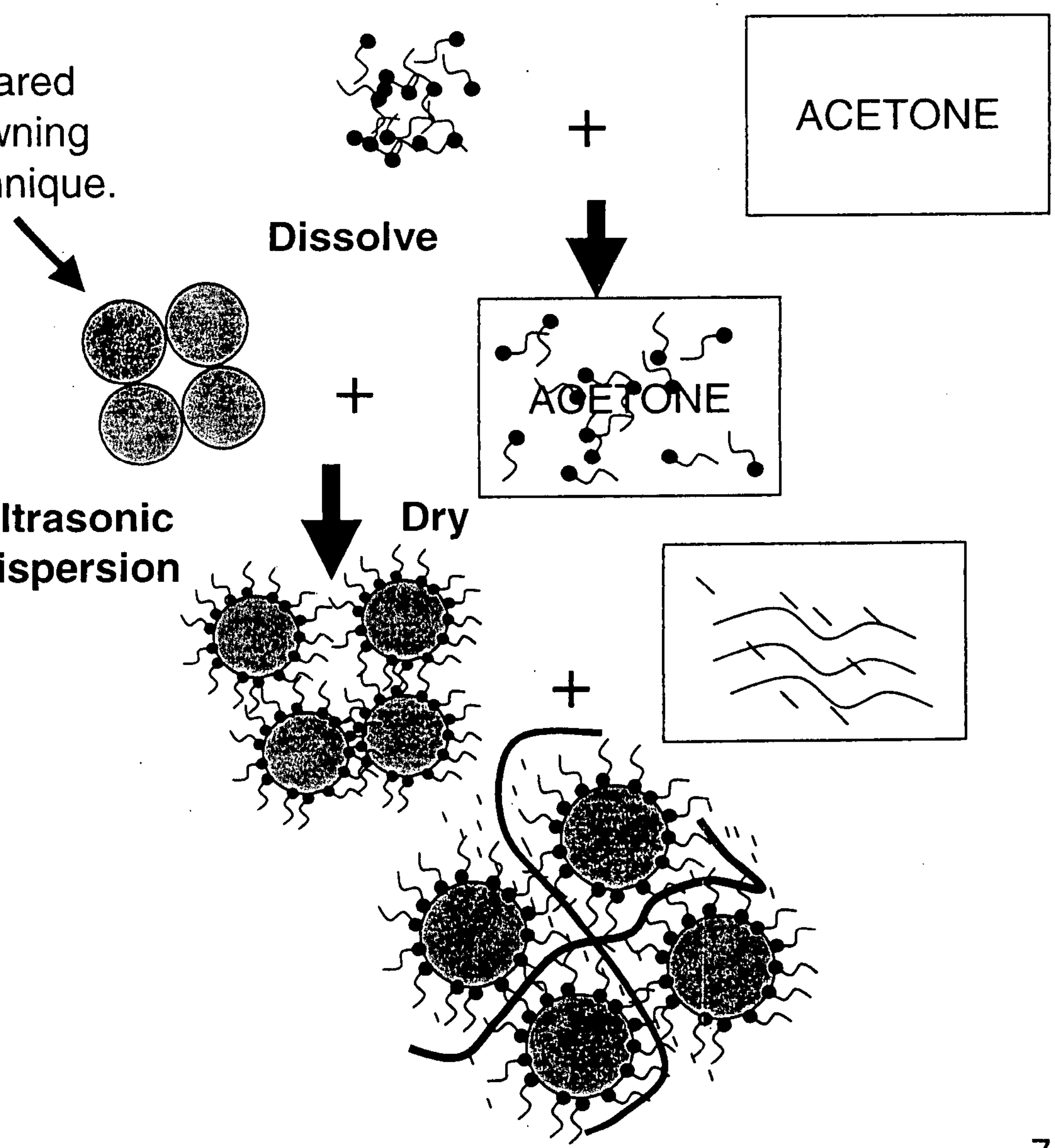
Thinner: Adjust the Paste Viscosity to Fit for Screen/Stencil Printing.

# TWO-STEP PROCEDURE

The nano-scale silver powder directly obtained commercially, and has compared price with micrometer silver powder owning To the commercialized nanosilver technique.

Particle Dispersion

Paste Quality Adjust



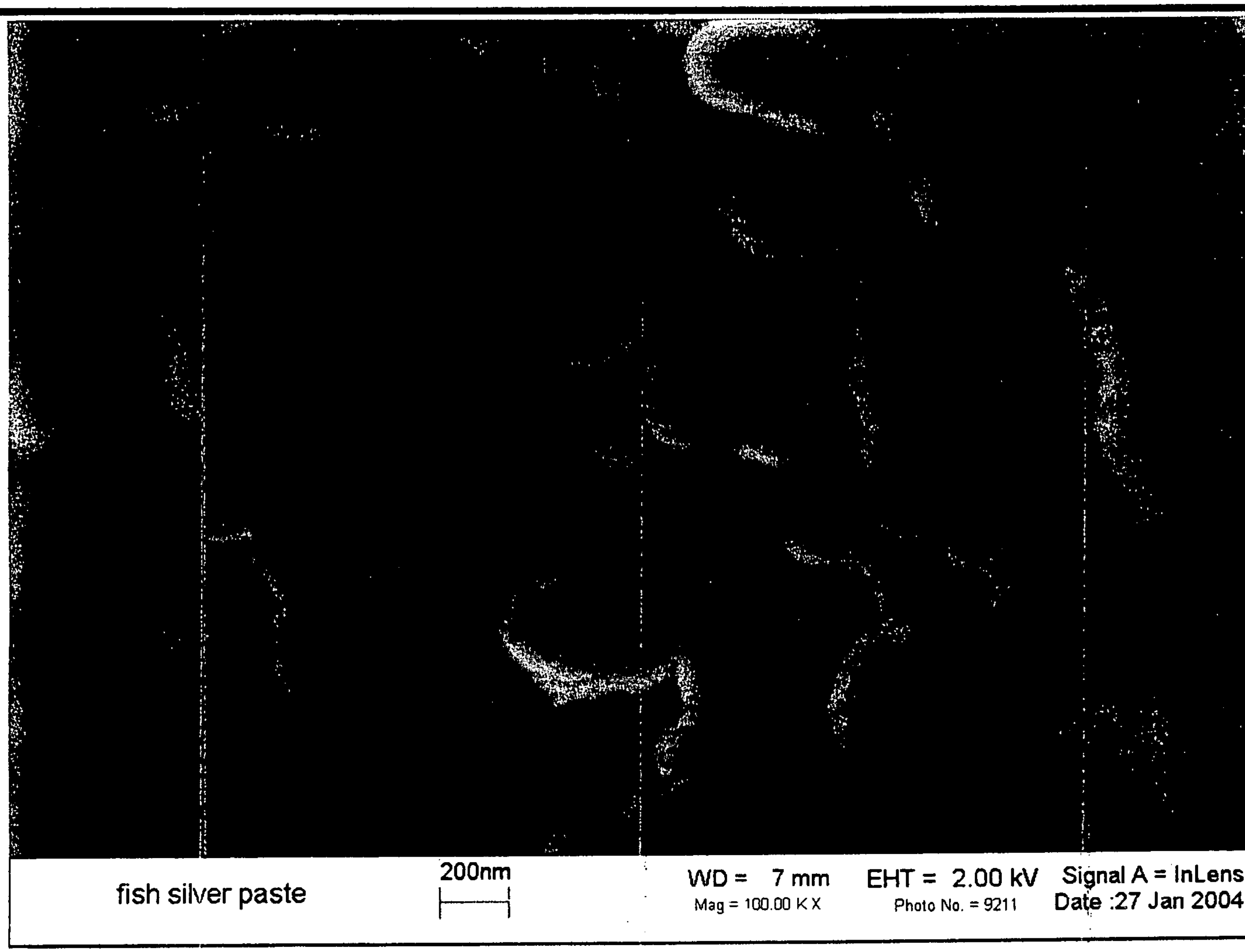
Advantages:

- Particles disperse and paste quality adjust are separated, process is much easier to control;

- The additional acetone significantly help fatty acid disperse silver particles during ultrasonic process;

- The nanopolar acetone easily separated from mixture of silver plus fatty acid without centrifuge.

# NANOSILVER DENSIFICATION




**Animation** of nanoscale silver was sintered/densified to form the interconnection by electron beams in several seconds and simultaneously observed by scanning electron microscopy.

Virginia Tech

# THERMAL PROPERTIES COMPARISION

| Property | Pb-Sn Solder | Sintered nanosilver | Pure Ag |
|---|---|---|---|
| Therm. Conduc. $\kappa$ (W/m-K) | 40 -- 60 | 210 | 419 |
| Melting Point (°C) | 120 - 350 | 961 | 961 |

Other properties (electrical conductivity / mechanical strength) and reliability are on the way to test.

From the pressure-assisted silver sintering results and theoretical analysis, the sintered nanosilver should have much better properties (electrical conductivity / mechanical strength) and reliability.